PREPARATION OF LIQUID FUELS FROM WASTE PLASTICS

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

Bachelor of Technology

In

Chemical Engineering

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2008

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CERTIFICATE

This is to certify that the thesis entitled, "**PREPARATION OF LIQUID FUELS FROM WASTE PLASTICS**" submitted by Mr. Avinash Mohapatra & Mr. Manpreet Singh in partial fulfillments for the requirements for the award of Bachelor of Technology Degree in Chemical Engineering at National Institute of Technology, Rourkela is an authentic work carried out by them under my supervision and guidance. To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

Date: 12-5-08

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ABSTRACT

Waste plastics from municipal solid waste were collected. It was be sorted based on the types like (HDPE, LDPE, PVC etc). They were graded into nearly uniform size by crusher, cutter and shredder. The graded feed was heated just to melt it so that extraneous impurities such as hard metal, clay, sand, glass etc settles in the bottom of the melter, which was removed periodically. The gaseous product during melting can be either dissolved in suitable solvent or incinerated to produce heat. The modern plastic along with catalyst is sent to a reactor, which is maintained at temperature between 350-600 ^{0}C and atmospheric pressure. The vapor which comes out of the reactor can be distilled to obtain different fractions of petroleum products. The different fractions dependent upon type of feed, catalyst/feed ratio, temperature and time of heating. Catalyst and the different products are characterized for there usefulness. The various properties of the products obtained were than tested and compared with the actual values for petroleum range products.

Acknowledgement

We would like to thank Dr. R.K.Singh for his co-operation, guidance and encouragement in the completing the project. We would like to thank Head of the Department Chemical Department, Dr. K.C. Biswal for the kind support and cooperation for allowing us to work in the department. I am also very grateful to all the laboratory assistants and all the non-teaching staff at Chemical engineering Department for helping us when required without them the completion of the project would not be a success.

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CHAPTER 1

1. INTRODUCTION

Plastics have become an indispensable part of today's world. Due to their light weight, durability, energy efficiency, coupled with a faster rate of production and design flexibility, these plastics are employed in entire gamut of industrial and domestic areas. Plastics are non-biodegradable polymers of mostly containing carbon, hydrogen, and few other elements such as chlorine, nitrogen etc. Due to its non-biodegradable nature, the plastic waste contributes significantly to the problem of Municipal Waste Management. The production of plastics is significantly growing. Nowadays the plastic production is more than 200MT worldwide annually. According to a nation wide survey, conducted in the year 2004, approximately 10,000 tones (ten thousand tones) of plastic waste were generated every day in our country, and only 60% of it was recycled, balanced 40% was not possible to dispose off. So gradually it goes on accumulating, thereby leading to serious disposal problems. In India, plastics consumption grew exponentially in the 1990s. During the last decade, the total consumption of plastics grew twice as fast (12% p.a.) as the gross domestic product growth rate based on purchasing power parities (6% p.a.). The current growth rate in Indian polymer consumption (16% p.a.) is clearly higher than that in China (10% p.a.) and many other key Asian countries. The average Indian consumption of virgin plastics per capita reached 3.2 kg in 2000/2001 (5 kg if recycled material is included) from a mere 0.8 kg in 1990/1991. [10]

1.1 Need for concern:

The increasing quantities of plastics waste and their effective and safe disposal has become a matter of public concern. The increasingly visible consequences of indiscriminate littering of plastic wastes (in particular plastic packaging wastes and discarded bags) has stimulated public outcry and shaped policy. Littering also results in secondary problems such as drains becoming clogged and animal health problems (both domesticated and wild). As a consequence, many big cities (e.g. Mumbai, Bangalore) and some of the states (e.g. Delhi, Uttar Pradesh) have already banned the use of thin plastic

bags. The consumption of plastics will increase about six-fold between 2000 and 2030. The share of polyolefins in India will remain at about 60%, a percentage comparable to that of Western Europe. **[10]**

1.2. Types of plastic: [3]

Table 1.1- types of plastic

Type I	Recyclable	Polyethylene Terephthalate	Beverages
Type II	Recyclable	High density Polyethylene	milk, detergent, oil bottles, toys, containers used outside parts and plastic bags
Type III	Recyclable(uncommon)	Polyvinyl chloride	Food wrap, vegetable oil, bottles, automotive parts
Type IV	Recyclable	Low density polyethylene	Plastic bags, shrink wraps, garment bags
Type V	Recyclable	Poly-propylene	Refrigerated containers, some bags, most bottle tops, some carpets.

CHAPTER 2

2. LITERATURE REVIEW:

Following works have been already done in this field by the following scientists:

2.1. Prof. Alka U. Zadgoaonkar

2.1.1. Prof. Alka U. Zadgoaonkar has invented a process system, which converts polymeric materials into liquid, solid and gaseous fuel. The process consists of two steps:

2.1.1.1. Random De-polymerization: Loading of waste plastics into the reactor along with the catalyst system. Random de-polymerization of the waste plastics occurs when plastics are heated along with catalyst.

2.1.1.2. Fractional distillation: Separation of various liquid fuels by virtue of the difference in their boiling points.

2.1.2 The process description:

The waste plastic is sorted based on the physical properties such as hardness, softness, films etc. Size reduction is carried out using shredder and cutter and graded to uniform size. The graded feed is mixed and fed to the melting vessel through a pre heater feeder and heated to 175-250 °C. The impurities such as clay, metals, glass etc settles at the bottom and sent to water column for separation of HCl gas and gaseous hydrocarbons. The molten plastic is sent to main reactor which is maintained at (300-350) °C and atmospheric pressure. The reaction takes place in presence of coal and catalyst to convert the molten plastic into hydrocarbons. The gaseous hydrocarbon shall be condensed and separated into liquid and gas streams. [8]

2.2. Jerzy Walendziewski and Mieczysaw Steininger:

Jerzy Walendziewski and Mieczysaw Steininger from Wrocław University of Technology, Wrocław, Poland cracked waste samples of polyethylene and polystyrene thermally or in the presence of catalyst and hydrogen in closed autoclaves. The obtained products were submitted to analysis; unsaturated hydrocarbons in gasoline and diesel fuel range boiling were hydrogenated over platinum catalyst. It was stated that the optimum thermal cracking temperature of waste polyolefines is 410–430°C, in the case of catalytic

process lower temperature, ca. 390°C, can be used, with reaction time ca. 1.5 an hour. More than 90% yield of gas and liquid fractions with b.p.<360°C was attained. The dependencies between process parameters, feed composition and product yield as well as composition of the obtained fuel fractions were found. On the basis of the obtained results Jerzy Walendziewski and Mieczys Steininger reported a hypothetical continuous process of waste plastics processing for engine fuel production was presented.

2.2.1. Materials used by them:

Waste samples of polyethylene and polystyrene were used as raw material.

2.2.1.1. Cracking of polyolefines was carried out in autoclaves (volume: 1 dm3) placed in a rotary kiln (10 min^{-1}).

2.2.1.2. Pressure and temperature measurement systems as well as the systems of pressurize and depressurize.

2.2.1.3. Two kinds of catalysts were applied in these studies: hydro cracking catalyst, containing NiW and 10% of HY zeolite, and waste commercial fluid cracking catalyst.

2.2.2. Cracking of Waste plastic:

At atmospheric pressure polymer cracking was carried out in a batch reactor(100 gm feed) in presence of (0-10%) of cracking catalyst in a glass reactor equipped with heating device and a distillation cooler. Otherwise if, autoclaves were used than, the plastic scrap feeds (25–100 g) were placed in the autoclaves and then if necessary solvent such as propane–butane, heptane or diesel fuel was added. A part of the experiment was carried out without any solvent but with addition of cracking or hydrocracking catalysts (0.3–0.5 wt% in relation to the weight of plastic). The autoclaves with plastic feeds were fed with hydrogen up to the pressure ranging from 2 to 5 MPa. The autoclaves were rotated and heated up to the reaction temperature, 370–450°C, ca. 3 h and next their temperature was held constant for 0.5–2 h. After finishing of the reaction cycle the autoclaves content was cooled to ambient temperature, the valves were opened and gaseous products of reaction were directed to gas containers, submitted for measuring volume, density and chemical composition using gas chromatography. Liquid and solid parts of autoclaves content was weighed and submitted for determination of normal distillation, gas

chromatography and bromine number. Molecular mass of solid and liquid products residue was determined. During plastics processing, after finishing the tests, autoclaves were cooled down to temperature 360°C and depressurised. Vapours of reaction products of this temperature were flowing through water cooler, gas products were collected in gas reservoir and liquids in receiver.

In the next step liquid products of polyolefines cracking, gasoline fraction with boiling point <180°C, was submitted for hydrogenation using noble metal based catalysts in flow micro-reactor apparatus (3 cm^3 of catalyst, 3 MPa, 280–320°C). The hydrogenation and hydrocracking studies were carried out in continuous flow apparatus (OL: 115) equipped with feeding, temperature controlling, as well as gas and liquid products receiving systems.

2.2.3. Determination of physicochemical properties of the obtained products:

- Chemical composition of gas products was determined by chromatography method, gas chromatograph N503, FID detector, Porapak Q+S and 2.5 columns.
- Chemical and fraction composition of liquid gas products was determined by chromatography method, gas chromatograph CHROM 4, FID detector, capillary column, 30 m, phase OV-17.
- Normal distillation of liquid products of cracking of polyolefines was made according to Polish Standard PN-67/C-04010.
- Aromatics content in liquid products was determined by IR method, Carl Zeiss Jena apparatus, Model M80, measuring absorption band 1600–1610 cm−1 and calculating according to the formulae:

$$C_A\ (\%) = 0.22 + 10.4 * K_{1610}.$$

Bromine number, as an indicator of olefins content was determined according to ASTM-D 1491-60 (1971).

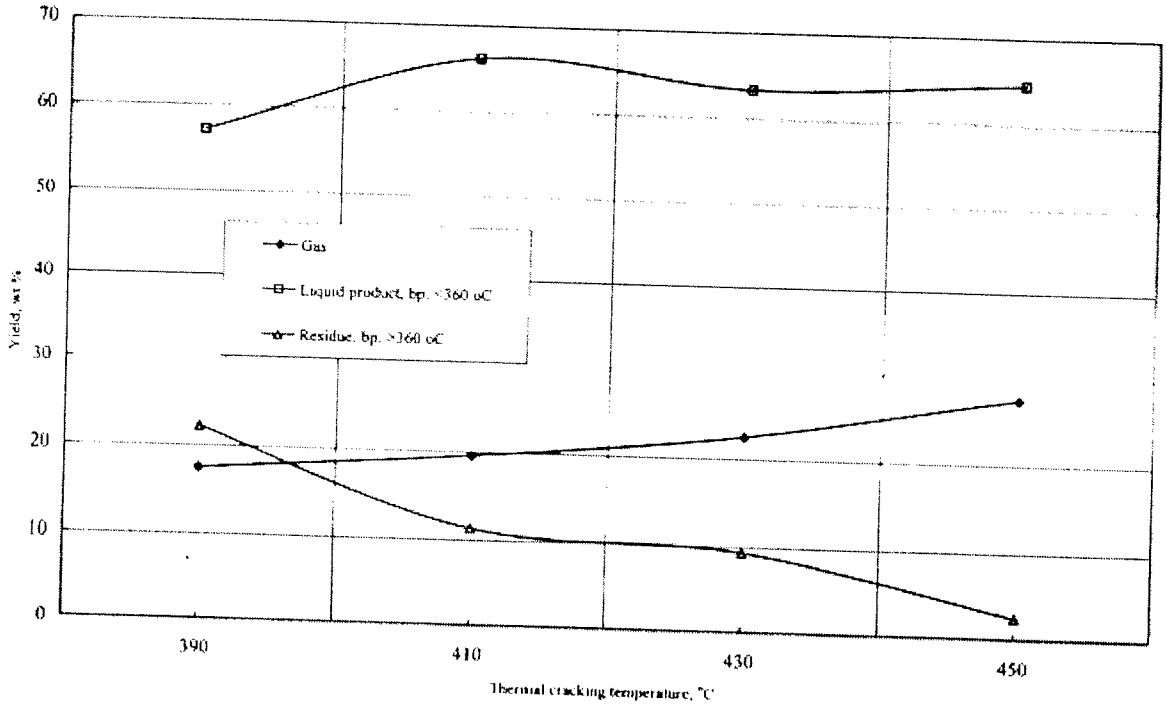


Fig. 2.1. Influence of reaction temperature on product composition of thermal cracking process of waste polyetheylene.

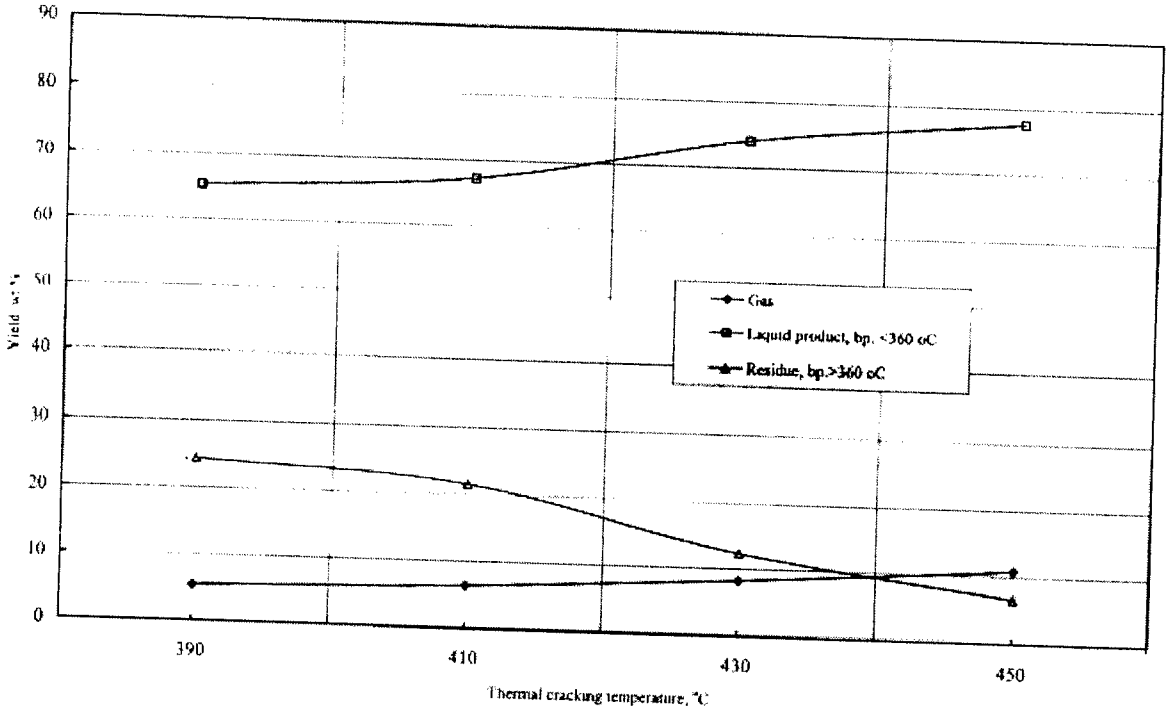


Fig. 2.2. Influence of reaction temperature on product composition of thermal cracking process of waste polystyrene.

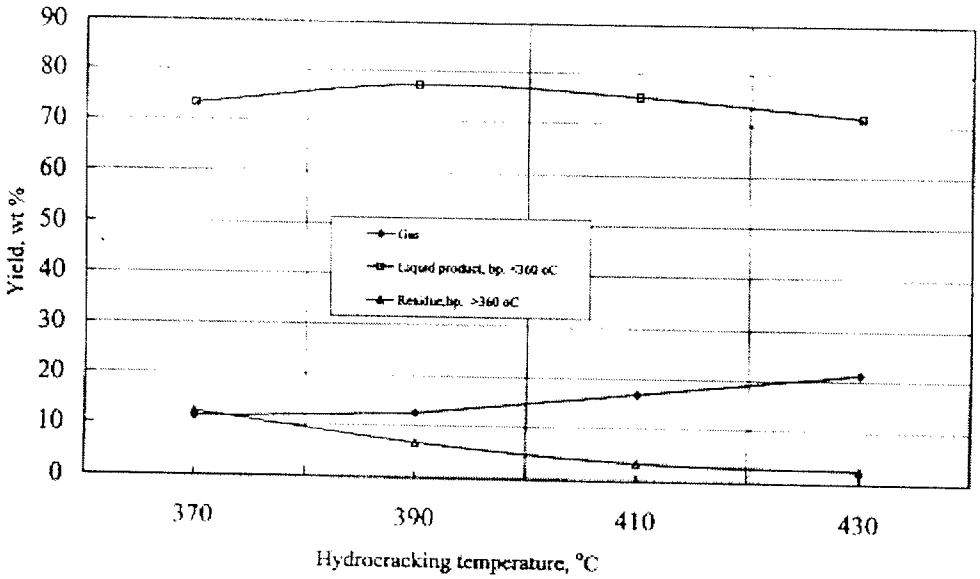


Fig.2.3. Influence of temperature on product composition of hydrocracking process of waste polyethylene

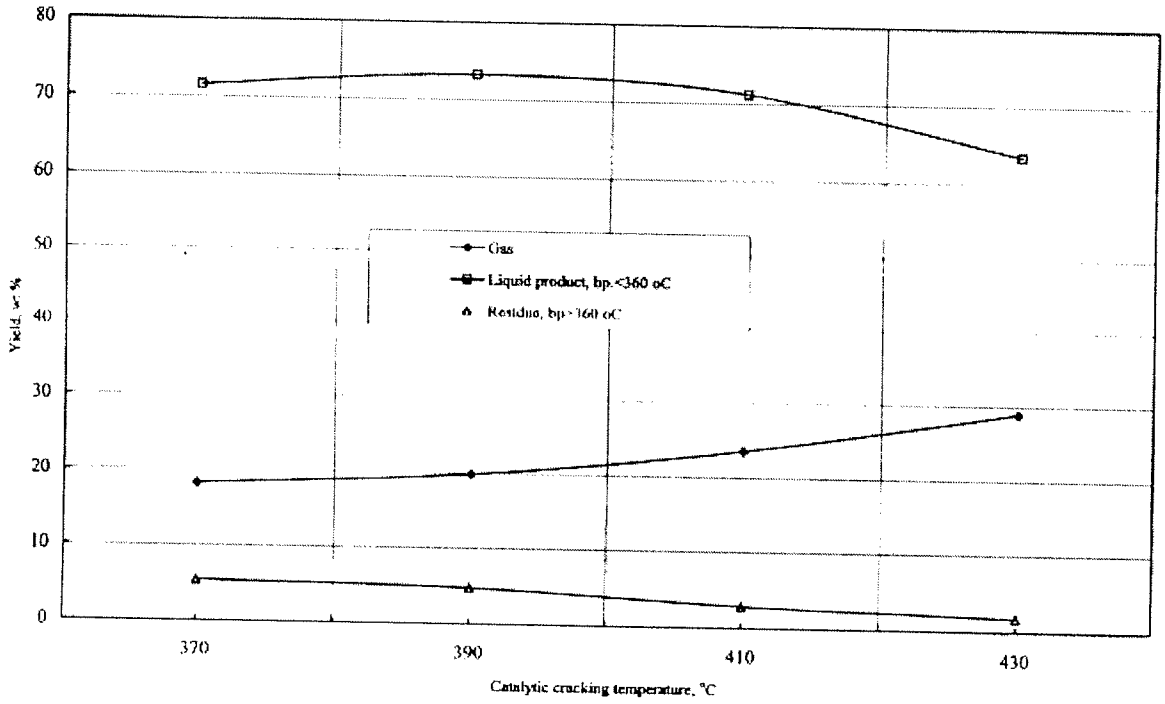


Fig.2.4. Influence of temperature on product composition of catalytic cracking process of waste polyethylene.

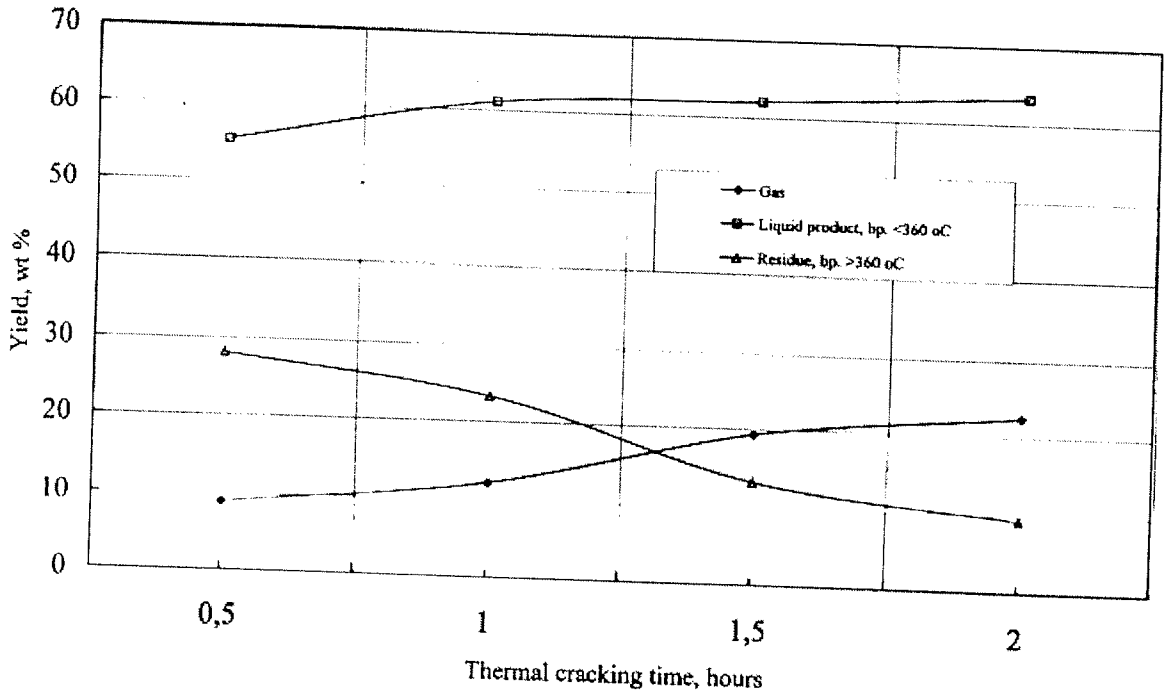


Fig.2.5. Influence of reaction time on product composition of catalytic cracking process of waste polyethylene (temperature: 430°C). [3]

2.3. N. Miskolczi, L. Bartha and Gy. Deák:

From the University of Veszprém three research scholars N. Miskolczi, , L. Bartha and Gy. Deák carried out Thermal degradation of polyethylene and polystyrene from the packaging industry over different catalysts into fuel-like feed stocks.

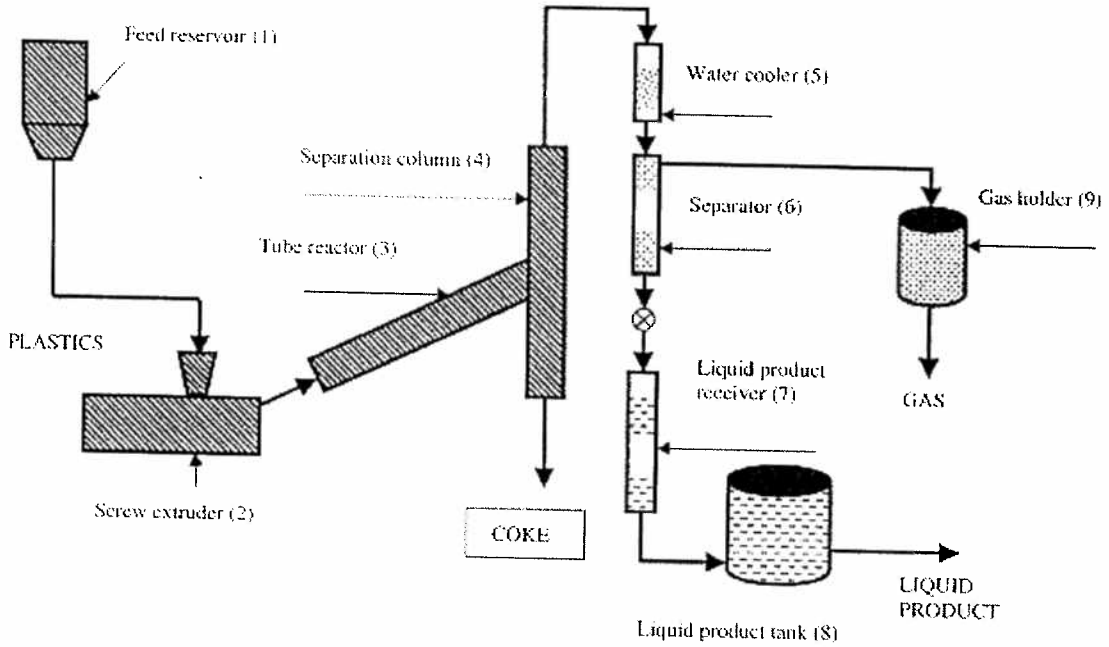
The catalytic degradation of waste plastics (polyethylene and polystyrene) was investigated in a batch reactor over different catalysts (FCC, ZSM-5 and clinoptillolite). The effects of catalysts and their average grain size on the properties of main degradation products (gases, gasoline, diesel oil) are discussed. The temperature range of 410–450 °C was used in the process. Both equilibrium FCC catalyst and natural clinoptilolite zeolite catalyst had good catalytic activity to produce light hydrocarbon liquids, and ZSM-5 catalyst produced the highest amount of gaseous products. Gases and liquids formed in cracking reactions were analyzed by gas chromatography. The liquid products consisted of a wide spectrum of hydrocarbons distributed within the C5–C28 carbon number range depending on the cracking parameters. The composition of hydrocarbons had linear non-

branched structure in case of polyethylene, while from polystyrene more aromatics (ethyl-benzene, styrene, toluene, and benzene) were produced. The yields of volatile products increased with increasing degradation temperature. The olefin content of liquids was measured with an infrared technique and an olefin concentration of 50–60% was observed. The concentration of unsaturated compounds increased with decreasing temperature, and in the presence of catalysts. The activation energies were calculated on the basis of the composition of volatile products. The apparent activation energies were decreased by catalysts and catalyst caused both carbon-chain and double bond isomerisation.

2.3.1. Process Description:

High temperature pyrolysis and cracking of waste thermoplastic polymers, such as polyolefines, polyethylene (PE), polypropylene (PP) and polystyrene (PS), are well known and environmentally accepted methods of their utilisation. This group of processes embraces thermal pyrolysis and cracking, catalytic cracking and hydro cracking in the presence of hydrogen. Pyrolysis is the typical chemical recycling process, enabling production of monomers, mainly ethylene, propene and butene from waste plastics. In case of cracking processes, their main products are fuels fractions, gaseous hydrocarbons and liquid mixtures of hydrocarbons boiling in the range of temperatures ~ 35–360 °C (gasoline and light gas oils) as well as the solid carbon residues, similar to coke. Numerous papers present the results of application of various acidic catalysts, such as silica alumina, zeolites (HY, HZSM-5, mordenite) or alkaline compounds such as ZnO, CaO and K_2O. An interesting method of polymers utilization is cracking, similar to the visbreaking of vacuum residue or catalytic cracking of vacuum gas oil (VGO) in the presence of various zeolites containing cracking catalysts. Some inventors propose cracking of melted polymers together with petroleum and carbon derived fractions or biomass with using of typical commercial and laboratory prepared catalysts. This type of the processes, application of catalyst of higher acidity (HY, ZSM-5, silica–alumina based catalysts) results mainly in C_5–C_{12} liquid hydrocarbons, while in case of thermal or process with the use of non-acid catalysts somewhat higher content of C_{12}–C_{22} compound

was also found.



2.6. Process Diagram

Increase in process temperature up to 685–715 °C and application of non-catalytic fluidized bed system for pyrolysis of mixture of municipal plastic wastes resulted in gaseous products, e.g. over 41 wt.% in that olefins 15% and aromatic (BTX) containing liquid products. The application of water steam as fluidization agent gas enabled higher C_2–C_3 olefins yield, from 48% to 60% accompanied by decrease in BTX yield from 24 to 11 wt.% .

Extent of conversion of plastics or plastic derived waxes into light engine fuels can be enlarged by the application of stable hydrocracking catalysts. In such a case, the task of catalyst and hydrogen presence is not only hydrocracking of long paraffin or polymer chains but also hydrogenation of olefins. The obtained products are of particularly good quality. The main drawback of these proposals, though, is the high investment costs. All the plants, fluid catalytic cracking and hydrocracking, can be economically feasible in refinery scale and their efficiency would be low in case of waste plastics processing.

On the one hand, the principal problem is that in the course of the cracking process all catalysts deactivate very quickly. If we consider very expensive catalysts, e.g. with

zeolites as the acidic components, the cost of waste plastics cracking process will be so relatively high that even economically unacceptable due to the fact that the whole catalyst is contained in coke and therefore cannot be recovered and regenerated. On the other hand, though, quick deactivation of the catalysts by coke deposition is characteristic of the cracking processes. Therefore, the best solution would be fluidized bed catalytic cracking similar to the fluid catalytic cracking (FCC) process in refinery industry with continuous regeneration of the catalyst. It enables continuous exchanging, regeneration and recirculation of the applied catalysts. However, this solution cannot be satisfactory for small cracking plants of waste plastics. British Petroleum proposed fluid cracking of waste plastics in the cracking plant of 100,000 tons output per year, but it seems to be the amount to small in order to consider the plant operation profitable.

Therefore, the selection of the effective cracking reactor for waste plastic processing is the problem of the utmost importance. Carbonaceous solid residue is one of the cracking products (10% or more in waste plastics cracking) and its continuous removal from the reactor is necessary. It was earlier stated that fluidized bed reactor is the best solution for large scale refinery cracking since it ensures coke removing. There were proposed different cracking reactors for processing of plastics or their mixture with other materials in small scale, but they did not enable the interrupted run and continuous coke removal. The potentially effective solution is application of a tube reactor with an internal multifunction screw mixer that removes coke from cracking reactor walls and then from the reactor. In this paper, I present results of thermal cracking of mixtures of the selected polyolefines in a continuous flow, laboratory cracking tube reactor with a screw internal mixer as well as other unit elements such as a screw extruder as feeding system, a gas–liquid separator and gas and liquid products receivers. It is shown that the application of this reactor type allows for thermal cracking of the mixtures of various polyolefines in continuous mode giving liquid and gas hydrocarbon products with 80–95% efficiency in relation to the feed. Solid product of the process is continuously being removed from the reaction zone. It is thermal, non-catalytic process. The positive factor of the application of cracking catalyst is lowering of the process temperature.

2.4. Properties of various fuels [6]

2.4.1. Gasoline:

Gasoline is a mixture of hundreds of hydrocarbons, many of which have different boiling points. Thus gasoline boils or distills over a range of temperatures, unlike a pure compound –water, for instance, that boils at a single temperature. These are the liquid fuels used in reciprocating, spark ignition combustion engines. These are broadly of two types, namely, motor gasoline and aviation gasoline. Motor gasoline is a mixture of low boiling hydrocarbons with the final boiling point of 215 °C. It is made in a refinery by blending a number of products such as

i. Straight run gasoline from distillation of crude oil
ii. Cracked gasoline produced by the cracking of gas
iii. Reformate obtained by the reforming of heavy naphtha
iv. Natural gasoline etc.

Natural gasoline and liquefied petroleum gas are sources of butane. Aviation gasolines are composed mostly of isoparaffins alkylates and aromatic reformats.

Specifications for motor gasoline:

Table 2.1:- [11]

Characteristics	83 octane	93 octane
Colour, visual	Orange	Red
Octane number(research),min	83	93
Lead content(g/l), max	0.56	0.8
Distillation		
i. Initial boiling pt. °C	-	-
ii. Recovery upto 70 °C(% vol)	10	10
iii. Recovery upto 125 °C(% vol)	50	50
iv. Recovery upto 180 °C(% vol)	90	90
v. Final boiling pt. °C, max	215	215
vi. Residue, % by vol., max	2	2
Reid vapour pressure at 38°C,kgf/cm^2	0.7	0.7
Sulphur, total % by weight, max	0.25	0.2
Residue on evaporation, mg/100 ml,	4.0	4.0

max		
Oxidation stability, mins, minimum	360	360
Copper strip test corrosion for 3 hrs at 50°C	Not worse than no. 1	
Density at 15 °C	Vary from 0.735 to 0.755 g/cc	

A gasoline's distillation profile or distillation curve is the set of increasing temperatures at which it evaporates for a fixed series of increasing volume percentages – 5, 10, 20, 30 percent, etc. – under specific conditions. (Alternatively, it may be the set of increasing evaporation volume percentages for a fixed series of increasing temperatures.) Figure 2.9 shows the distillation profiles of average conventional summer and winter gasolines. A distillation profile also is shown for a summer reformulated gasoline containing ethanol.

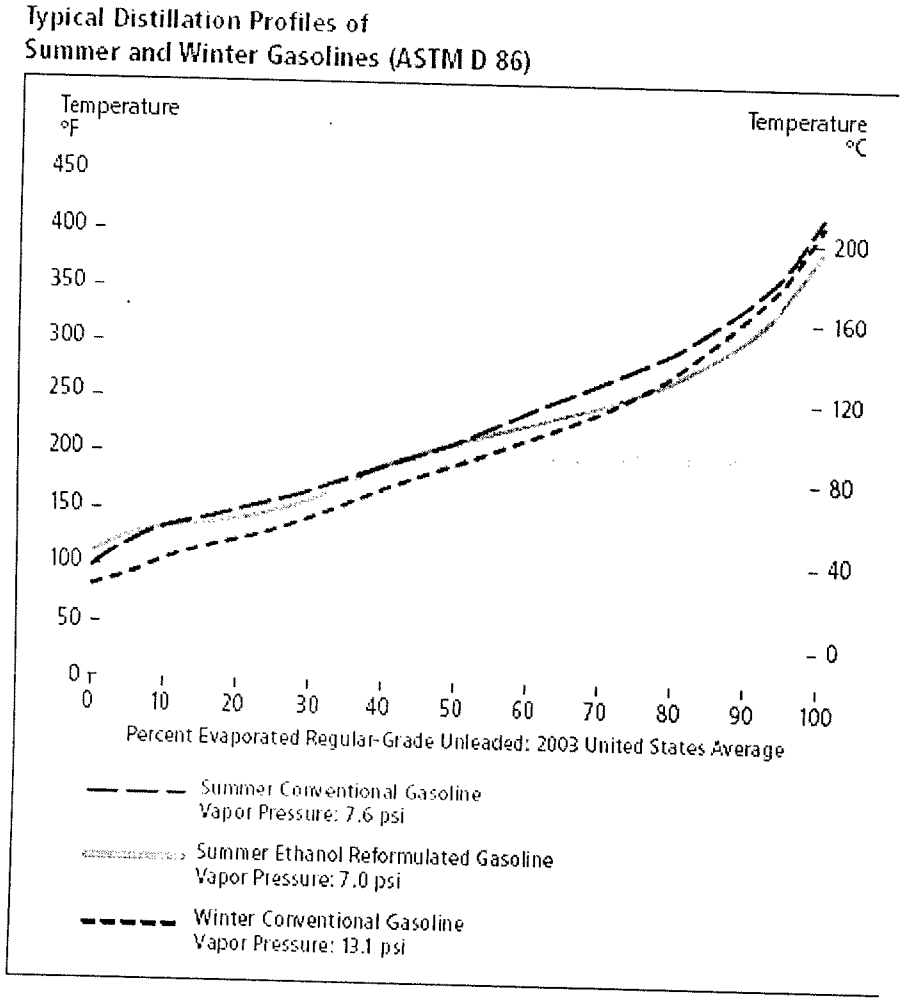


Fig 2.7 [2]

2.4.2. Diesel Fuels: Diesel fuel keeps the world economy moving. From consumer goods moved around the world, to the generation of electric power, to increased efficiency on farms, diesel fuel plays a vital role in strengthening the global economy and the standard of living.

Table 2.2 Specifications of Diesel:

Property	Test Method	S5000* No. 1-D	S5000* No. 2-D	No. 4-D
Flash Point, °C (°F), min	D 93	38 (100)	52 (125)	55 (130)
Water and Sediment, % volume, max	D 2709 D 1796	0.05	0.05	– 0.50
Distillation Temperature, °C (°F), 90% Volume Recovered: min max Or Simulated Distillation, °C (°F) (Does not apply to No. 1-D S5000 or No. 2-D S15) 90% Volume Recovered: min max	D 86 D 2887	 288 (550) 304 (572)	 282 (540) 338 (640) 300 (572) 356 (673)	
Kinematic Viscosity, mm^2/sec at 40°C (104°F): min max	D 445	 1.3 2.4	 1.9 4.1	 5.5 24.0
Ash, % mass, max	D 482	0.01	0.01	0.10
Sulfur, ppm (µg/g), max % mass, max % mass, max	D 5453 D 2622 D 129	15 0.05 0.50	15 0.05 0.50	– – 2.00
Copper Strip Corrosion Rating, max After 3 hours at 50°C (122°F)	D 130	No. 3	No. 3	–
Cetane Number, min One of the following must be met: (1) Cetane Index, min (2) Aromaticity, % volume, max	D 613 D 976-80 D 1319	40 40 35	40 40 35	30 – –
Cloud Point, °C (°F), max	D 2500	Varies	Varies	–

The fuel grades S15, S500, and S5000 refer to the maximum sulfur content e.g., S15 refers to diesel fuel with a maximum sulfur content of 15 ppm).

2.4.2.1. Diesel Fuel Chemistry:

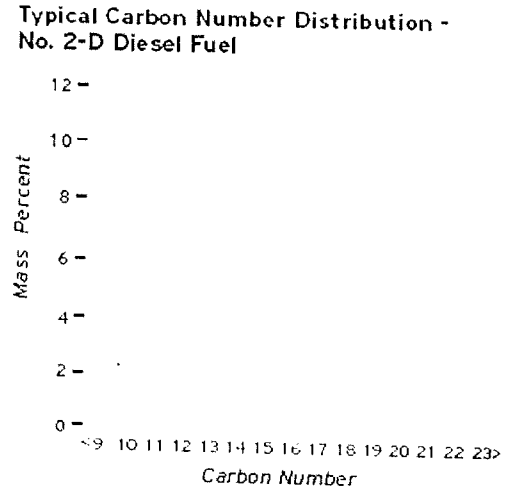


Figure 2.8

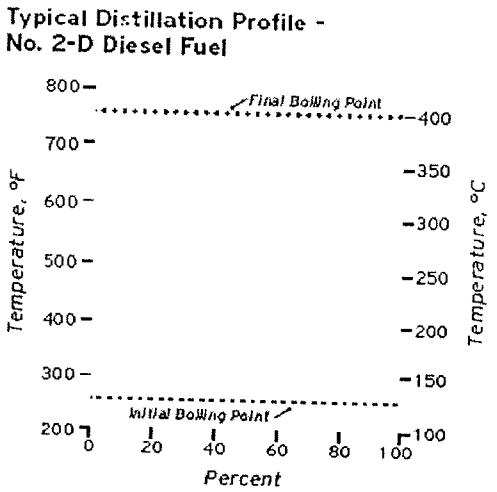


Figure 2.9

Figure 2.7 illustrates a typical carbon number distribution for No. 2-D diesel fuel, and Figure 2.8 shows a typical distillation profile. Diesel fuel is a very complex mixture of thousands of individual compounds, most with carbon numbers between 10 and 22. Most of these compounds are members of the paraffinic, naphthenic, or aromatic class of hydrocarbons; each class has different chemical and physical properties. Different relative proportions of the three classes is one of the factors that make one diesel fuel different from another. The following discussion explains how properties of the three classes influence the properties of the whole fuel and affect its performance in a diesel engine.

2.4.2.2. Cetane number:

Cetane number also varies systematically with hydrocarbon structure. Normal paraffins have high cetane numbers that increase with molecular weight. Isoparaffins have a wide range of cetane numbers, from about 10 to 80. Molecules with many short side chains have low cetane numbers; whereas those with one side chain of four or more carbons have high cetane numbers. Naphthenes generally have cetane numbers from 40 to 70. Higher molecular weight molecules with one long side chain have high cetane numbers; lower molecular weight molecules with short side chains have low cetane numbers. Aromatics have cetane numbers ranging from zero to 60. A molecule with a single

aromatic ring with a long side chain will be in the upper part of this range; a molecule with a single ring with several short side chains will be in the lower part.

2.4.3 Fuel Stability Additives

Fuel instability results in the formation of gums that can lead to injector deposits or particulates that can plug fuel filters or the fuel injection system. The need for a stability additive varies widely from one fuel to another. It depends on how the fuel was made – the crude oil source and the refinery processing and blending. Stability additives typically work by blocking one step in a multi-step reaction pathway (see page 37). Because of the complex chemistry involved, an additive that is effective in one fuel may not work as well in another.

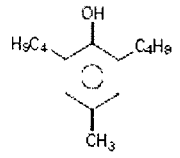
If a fuel needs to be stabilized, it should be tested to select an effective additive and treat rate. Best results are obtained when the additive is added immediately after the fuel is manufactured. S15 diesel fuels will probably be more thermally stable, but may be prone to peroxide formation during storage.

2.4.3.1. Antioxidants

One mode of fuel instability is oxidation. Oxidation takes place when oxygen, in the small amount of dissolved air, attacks reactive compounds in the fuel. This initial attack sets off complex chain reactions.

Antioxidants work by interrupting the chain reactions. Hindered phenols and certain amines, such as phenylenediamine, are the most commonly used antioxidants. They typically are used in the concentration range from 10 to 80 ppm. Butylated hydroxyltoluene (BHT) (Barcelona, Spain) and tert-butyl hydroquinone (TBHQ) are some of the commonly used antioxidants to increase the durability test of oil.

Antioxidant



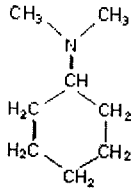
2,6-Di-t-butyl-4-methyl phenol

Fig 2.10 Antioxidant

2.4.3.2. Stabilizers

Acid-base reactions are another mode of fuel instability. The stabilizers used to prevent these reactions typically are strongly basic amines and are used in the concentration range from 50 to 150 ppm. They react with weakly acidic compounds to form products that remain dissolved in the fuel and do not react further.

Stabilizer



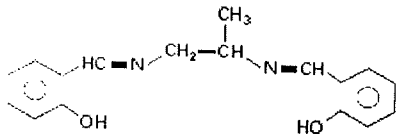
N, N-Dimethylcyclohexyl amine

Fig 2.11 Stabilizers

2.4.3.3. Metal Deactivators

When trace amounts of certain metals, especially copper and iron, are dissolved in diesel fuel, they catalyze (accelerate) the reactions involved in fuel instability. Metal deactivators tie up (chelate) these metals and neutralize their catalytic effect. They are typically used in the concentration range from 1 to 15 ppm.

Metal Deactivator



N, N-Disalicylidene-1,2-propanediamine (DMD)

Fig 2.12 Metal deactivator

2.4.3.4. Dispersants

Multi-component fuel stabilizer packages may contain a dispersant. The dispersant doesn't prevent the fuel instability reactions; however, it does disperse the particulates that form preventing them from clustering into aggregates large enough to plug fuel filters or injectors. Dispersants typically are used in the concentration range from 15 to 100 ppm.

2.5. Possible tests to ensure and confirm the presence of liquid fuels:

2.5.1. Distillation Profile: ASTM D 86 – Test Method for Distillation of Petroleum Products

Procedure:

A 100 mL sample is placed in a round bottom flask and heated at a rate specified for samples with its vapor pressure characteristics. Temperatures are recorded when the first drop is collected (initial boiling point), at recovered volumes of 5 mL, 10 mL, every subsequent 10 mL interval to 90 mL, 95 mL and at the end of the test (end point). For gasoline samples, the temperatures associated with each incremental volume percentage recovered are converted to temperatures for each incremental volume percentage evaporated by correcting for any sample loss during the test.

2.5.2. Copper Strip Corrosion:

ASTM D 130 – Test Method for Detection of Copper Corrosion from Petroleum Products by the Copper Strip Tarnish Test.

Procedure:

D 130 can be used to detect the presence of free sulfur or reactive sulfur compounds. In this test method, a polished copper strip is immersed in 30 mL of gasoline and heated to 50°C (122°F) for 3 hours. The test strip is compared to standard strips and reported on a scale of one to four (one being best).

It is becoming clear that as sulfur levels in gasolines are forced lower, many sulfur species that actually provided protection for copper surfaces are being greatly reduced or eliminated. In extremely low sulfur content reformulated gasolines, levels of free sulfur or reactive sulfur compounds that would not have caused a failed copper strip test in conventional gasolines may now cause a failure.

This factor increases the urgency for minimizing contamination with even minor levels of free sulfur or reactive sulfur compounds in processing at the refinery.

2.5.3. Flash Point:

ASTM D 93 – Flash-Point by Pensky-Martens Closed Cup Tester

Procedure:

At least 75 milliliters are required for this test. The sample is stirred and heated at a slow, constant rate in a closed cup. The cup is opened at intervals, and an ignition source is moved over the top of the cup. The flash point is the lowest temperature at which the application of the ignition source causes the vapors above the liquid to ignite.

2.5.4. Viscosity:

ASTM D 445 – Kinematic Viscosity of Transparent and Opaque Liquids

Procedure:

The sample is placed in a calibrated capillary glass viscometer tube and held at a closely controlled temperature. The time required for a specific volume of the sample to flow through the capillary under gravity is measured. This time is proportional to the kinematic viscosity of the sample.

2.5.5. Aromaticity:

ASTM D 5186 – Determination of Aromatic Content of Diesel Fuels by Supercritical fluid Chromatography.

Procedure:

The sample is chromatographed on silica gel using supercritical carbon dioxide as the mobile phase to separate the aromatics from the rest of the sample and to separate the aromatics into monoaromatics and polycyclic aromatics.

2.5.6. Hydrocarbon types:

ASTM D 1319 – Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption

Procedure:

A small amount of sample is placed at the top of a special glass adsorption column packed with activated silica gel. The top layer of the silica gel in the column is treated with fluorescent dyes. Isopropyl alcohol is used to transport the sample and the fluorescent dyes down the column. Hydrocarbons are separated into bands of aromatics, olefins, and saturates according to their affinity for the silica gel. The fluorescent dyes are also selectively separated and make the boundaries of the aromatic, olefin, and saturate zones visible under ultraviolet light. The volume percentage of each hydrocarbon type is calculated from the length of each zone in the column.

2.5.7. Cloud Point:

ASTM D 2500 – Cloud Point of Petroleum Products

Procedure:

A clean clear sample is cooled at a specified rate and examined periodically. The temperature at which a haze is first observed is the cloud point.

2.5.8. Pour Point:

ASTM D 97 – Pour Point of Petroleum Products

Procedure:

A clean sample is first warmed and then cooled at a specified rate and observed at intervals of 3°C (5°F). The lowest temperature at which sample movement is observed when the sample container is tilted is the pour point.

2.5.9. Carbon Residue:

ASTM D 524 – Ramsbottom Carbon Residue of Petroleum Products or Conradson apparatus

Procedure:

The sample is first distilled (ASTM D 86) until 90 percent of the sample has been recovered. The residue is weighed into a special glass bulb and heated in a furnace to 550°C (1,022°F). Most of the sample evaporates or decomposes under these conditions. The bulb is cooled and the residue is weighed. [1]

CHAPTER 3

WORK DONE AND PROJECT DESCRIPTION

3.1 Description of our experimental setup:

Waste plastics from municipal solid waste were collected. It was being sorted based on the types like (HDPE, LDPE, and PVC etc). They will be graded into nearly uniform size by crusher, cutter and shredder. The next step can be either of the two processes **conventional** and **modified** one.

In the conventional process the graded feed is heated just to melt it so that extraneous impurities such as hard metal, clay, sand, glass etc settles in the bottom of the melting vessel, which is removed periodically. The gaseous product during melting can be either dissolved in suitable solvent or incinerated to produce heat. The modern plastic along with catalyst is sent to a reactor, which is maintained at temperature between 500-550 ^{0}C and atmospheric pressure. The vapor which comes out of the reactor can be distilled to obtain different fractions of petroleum products. The different fractions depend upon type of feed, catalyst/feed ratio, temperature and time of heating. Catalyst and the different products are characterized for there usefulness. In modified one, the catalyst can be added in the melting beginning of the process and in the melting vessel itself and no more addition of the catalyst is required in the further process. There are certain merits and demerits of both the process. The feed to catalyst ratio and be well controlled in conventional one unlike modified on one in which loss of catalyst may occur but uniformity is well maintained in modified on.

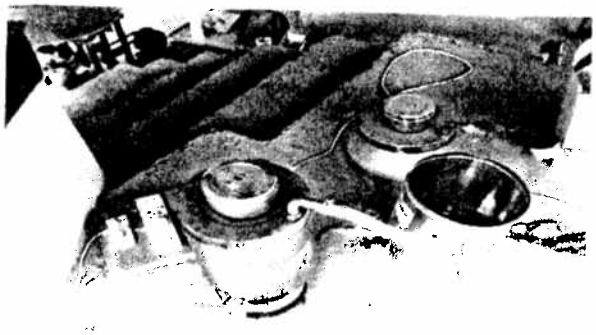


Fig 3.1- Melting vessel

Size reduction of the sorted feed is carried out using crusher, cutter and shredder and graded into uniform size using sieves (semi automatic). The graded feed is mixed and fed to Melting Vessel through pre heater feeder. In Melting Vessel, the feed is heated to 175-250 ^{0}C. The extraneous impurities such as hard metal, clay, sand, glass etc. settles in the bottom of the reactor, which shall be removed on periodic basis.

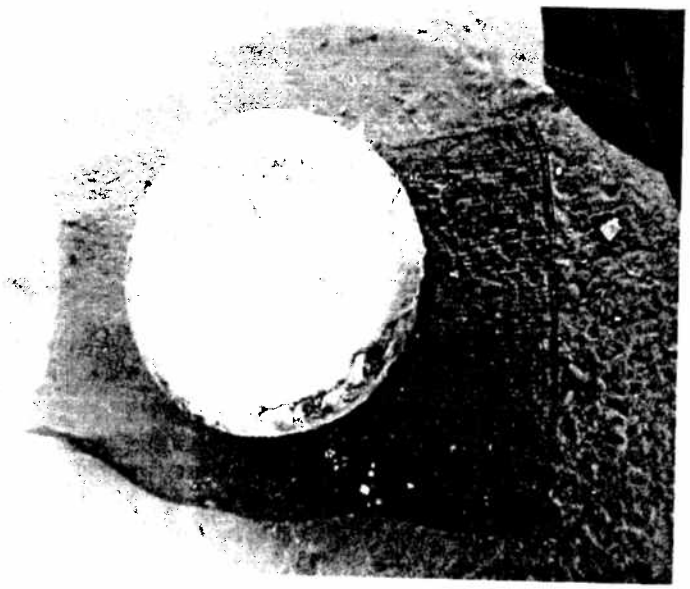


Fig 3.2- Molten plastic cake from melting vessel

The gaseous products from the molten plastic shall be subjected to separation of HCl gas and gaseous hydrocarbons. HCl gas is separated by absorption in a water column. The hydrocarbons free from HCl are separated and utilized independently. The molten waste plastic from dechlorination vessel is sent to a heated surge hopper and is fed into the main reactor, which is maintained at 500-550 ^{0}C and atmospheric pressure. The reaction takes place in the presence catalyst to convert the molten waste plastic into hydrocarbons. Small quantity of scavenger shall also be added, if required. The solid residue shall be taken out from the bottom of the main reactor on periodic basis by a specially designed conveyor occasionally.

The vapors coming from the reactor are enters into the condenser where these vapors are condenses to liquid hydrocarbon fuels. If we want we may distill these crude oils in a fractional distillation column. Thus the collected samples are to be tested by appropriate methods. In such a way we analyzed the products for their existence in the range of gasoline, diesel and petroleum.

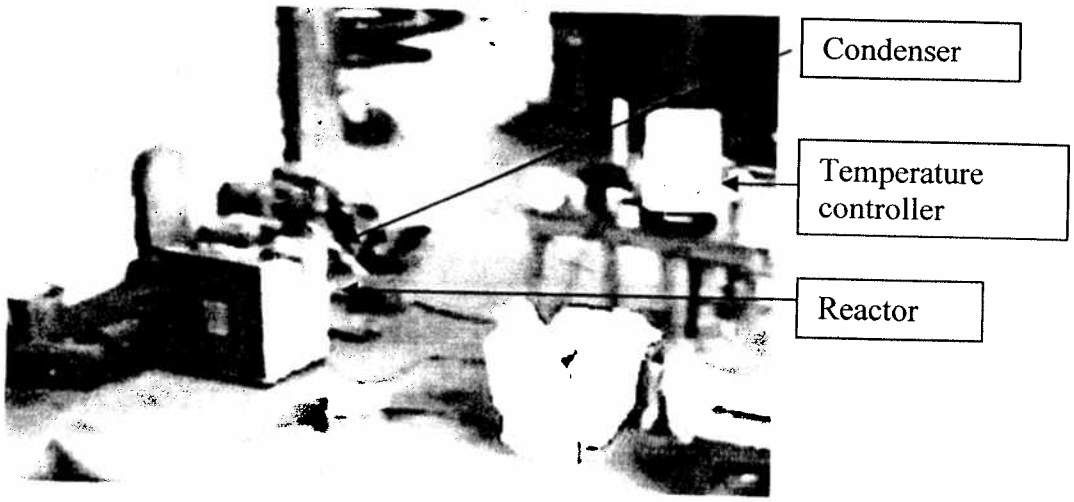


Fig 3.3:- Thermal cracking in the reactor with temperature controller

3.2. Tests performed on the products:

1. Density
2. Viscosity
3. Flash Point
4. Ash Content
5. Cloud Point
6. Pour Point
7. carbon residue

3.3. Detailed description:

The following tests were performed by us on the products obtained in the above experiments

3.3.1. Colour:

Procedure:

The sample is brought in sunlight and observed.

Observations:

The colour of lighter fraction is: light bluish (nearly colourless)

The colour of heavier fraction is: reddish orange

3.3.2. Density:

Procedure:

1. An empty specific gravitometer bottle is weighted.
2. 10 ml of the sample is taken in the bottle and weighted again.
3. The weight of the sample is found and density can be found.

Observations:.

Specific density of lighter fraction: 0.7185 g/cc

Specific density of lighter fraction: 0.8077 g/cc

3.3.3. Flash point:

Apparatus- Pensky-Martein Apparatus (closed cup with stirrer)

Procedure:-

1. The sample (either heavier or lighter one) is taken in the closed cup Pensky Martein apparatus.
2. It is heated and with every 5 °C rise check for the flash by igniting the wick near the opening.
3. Once the flash is observed, the temperature is decreased and minimum temperature at which flash is occurring, is noted which is the flash point.
4. It is done with the second sample in the same procedure.

Observations:

For heavier fraction, flash point- 38°C

For diesel, flash point- 38 °C

For lighter fraction, flash point- 25°C

Sources of error:

The cup should not be opened frequently as vapour won't accumulate and flash may not accumulate.

3.3.4. Ash content:

Apparatus: ceramic crucibles with oven or furnace

Procedure:

1. The sample is filled upto a level in crucible after weighing the empty crucible.
2. The sample (10 gms) is taken and placed in the oven.
3. The temperature is set at 500 °C for complete combustion.

4. The crucible is cooled and weighted.

Observation:

There is no ash content in either of the samples (heavier as well as lighter).

In diesel the ash content is 0.1.

3.3.5. Cloud point and pour point:

Apparatus: Ultra temperature refrigeration

Procedure:

1. The sample is taken in a glass tube and placed in a metallic tube.
2. This tube is then placed in ultra temperature refrigerator.
3. The temperature is fixed at -70 °C.
4. The sample ceases to flow at the temperature.

Observations:

The cloud point as well as the pour point are less than -70°C.

3.3.6. Viscosity:

Apparatus: Redwood viscometer with glass bulb of 50 ml.

Procedure:-

1. The sample is taken in the Redwood viscometer. The jacket is filled with normal water.
2. The temperature is increased by heating using heater and sample is continuously stirred.
3. The jacket temperature and sample temperature is maintained at 40°C.
4. The valve is opened and time is noted to fill up the glass bulb of 50 ml.
5. Procedure is repeated for other sample.

Calculation:

Viscosity, $\eta = AT - B/T$ cm^2/sec

Data shows:

Time (sec)	A	B
40-85	0.264	190
86-2000	0.247	65

Observations:

At 40°C,	time taken (sec)	viscosity (cm^2/sec)
Heavier fraction	34.67	3.673
Lighter fraction	26.68	-0.078

In case of diesel max viscosity is 2.4 cm^2/sec.

3.3.7. Carbon residue using Conradson apparatus:

Apparatus: Conradson apparatus with crucibles

Procedure:

1. The empty crucible (ceramic preferably) is taken and weighted.
2. 10 gm of the sample is poured in the crucible and kept in the Conradson apparatus.
3. The flame is put on and kept for half an hour till no gas or smoke is observed on the top of the chimney.
4. The crucible is weighted and the deposited carbon residue can be found.

Observations:

Lighter fraction:

Weight of empty crucible= 18.79 gm

Amount of lighter fraction taken= 10 gm

Amount of carbon residue= 18.84-18.79 = 0.5 gm

Heavier fraction:

Weight of the empty crucible= 19.88 gm

Amount of heavier fraction taken= 10 gm

Amount of carbon residue= 20.68-19.88 = 0.8 gm

The values found for the products range make it very clear that the products lie in the diesel and gasoline range.

3.4. Reactor design: [13]

A batch reactor operates once at a time. It requires extra time (i.e., downtime t_d) for loading and reloading the reactor.

Concentration of Species A:

$$V\frac{dC_A}{dt} = -kVC_A \tag{1}$$

Solving this ODE get

$$C_A = \text{Constant} \times \exp(-kt) \tag{2}$$

At $t = 0$, $C_A = C_{A\text{initial}}$, thus Constant $= C_{Ain}$

$$\frac{C_A}{C_{A_{in}}} = \exp(-kt) \tag{3}$$

As C_A approaches some small concentration CA,out , $t \rightarrow t_R$(residence time is time spent in the reactor). Therefore $t_R = k \times \ln (C_{A,in}/C_{A,out})$.

Production rate is Q =V/ total time =V/ (t_R+t_d)

Design calculations based on previous studies:

The reaction:-

Plastic + catalyst ⟶ liquid fuel + unreacted plastic, is a pseudo first order reaction.

Amount of feed (molten plastic) taken = 72 gms

Molecular weight of the HDPE = 38000 (avg)

Experimental volume of the reactor = 0.4 litre

Concentration of plastic in the reactor, C_{A0} = moles of feed/volume of the reactor

$(72/38000) / 0.4 \quad 4.736 \times 10^{-3}$ moles/litre

Concentration of the unreacted plastic, $C_A = (40/38000)/ 0.4 = 2.6315 \times 10^{-3}$ moles/litre

Conversion percent, $X_A = 44.43$ %,

Residence time, $t_R = 15$ mins $= 900$ sec.

Using eq(3), $K_t = \ln (C_{A0} / C_A)$

Rate constant can be found (as it is dependent on temperature) at 500 °C is found to be

$K = 6.529 \times 10^{-4}$ moles/litre/sec.

Since the conversion is unsatisfactory.

For high conversion, $X_A = 90\%$ (assume)

Residence time is found to be, $t_R = 3526.7$ sec

Volume of the rector required for such high residence time = (0.4/900) x 3526.7

= 1.56 litre

For feed of plastic = 72 gm, volume required is 1.56 litres for 90% conversion.

Total time per batch = $t_R + t_d = 3526.7 + 1800 = 5326.7$ sec

No. of batch per day = (24*3600)/5326.7 = 16.22 =16

The amount of liquid fuel produced is 90 cc.

For the feed of 1 ton of waste plastic,

Amount of feed = 10^6 gms,

Feed per batch = 10^6 / 16 = 62,500 gms per batch

Volume of reactor = (1.56/72) x 62500 = 1354.16 litre

Amount of liquid fuel manufactured per day = 78.125 litres.

CHAPTER 4

CHAPTER 4

RESULTS AND DISCUSSION

The project can be concluded in the following table 4.1:

	Lighter fraction	Heavier fraction
Color	Light bluish	Reddish orange
Density (gms/cc)	0.7185 g/cc	0.8077 g/cc
Flash point	25°C	38°C
Ash content	No ash	Negligible ash
Cloud point (°C)	< -70°C	< -70°C
Pour point (°C)	-70°C	-70°C
Viscosity (cm^2 / sec)	-0.078	3.673
Carbon residue (gm)	0.5	0.8

For regular gasoline, density varies from 0.735 to 0.755 g/cc and 0.755 g/cc density for premium gasoline. For diesel density is 0.85. The above readings gives the conclusion that both lighter and heavier fractions' density lie in there respective ranges. For diesel, flash point- 38 °C and heavier fraction is showing the same. However the flash point of gasoline range products have very low flash point can't matched with the lighter fractions. The ash content of diesel is less than 0.01(max). The above fractions have no ash. The cloud point and pour point show that the fractions have lower temperatures than those of diesel and gasoline. Kinematic viscosity of the diesel is 2.4 cm^2 / sec. The viscosity of the heavier fraction is much higher that shows further distillation and purification is required. At last the carbon content of lighter and heavier fractions are much higher than that of gasoline and diesel (0.15 gm of carbon residue on 10% distillation). The project shows some light on the possibility of manufacturing liquid fuels from waste plastics (which is non- biodegradable and dumped or incinerated) can become a very good future source of energy and power as we are on the verge of fuel shortages and environment imbalance.

CHAPTER 5

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